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Implications of Deposit Control Polymer Blending
to Water Treaters

Zahid Amjad, Ph.D. and Robert W. Zuhl, P.E.
Lubrizol Advanced Materials, Inc.
9911 Brecksville Road
Cleveland, OH 44141

Carbosperse™ K-700
Water Treatment Polymers

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Abstract

A wide variety of deposit control polymers (DCPs) have been developed for use as components of industrial water treatment programs to minimize both mineral scale formation and deposition of undesirable materials on equipment surfaces. Most DCPs incorporate one or more carboxyl containing monomers (e.g., acrylic acid, methacrylic acid, maleic acid) and many incorporate one or more specialty monomers (e.g., sulfonic acids, acrylamides, acrylate esters). Significant DCP performance differences have been well documented and attributed to factors including molecular weight, monomer ratios, and manufacturing processes and/or end groups. Although more expensive than homopolymers, copolymers typically provide several performance characteristics (e.g., calcium phosphate/phosphonate inhibition) not otherwise available. Water technologists seeking to optimize industrial water treatment formulation cost-performance frequently incorporate multiple DCPs. This paper presents laboratory screening test performance data (i.e., calcium phosphate inhibition, calcium carbonate inhibition, and iron oxide dispersion) for a ≈2k molecular weight (MW) polyacrylate (PAA), a high performance acrylate terpolymer (ATP), and a PAA/ATP blend. The observed performance differences are discussed in terms of polymer architecture and function.

Keywords: calcium phosphate, calcium carbonate, dispersion, inhibition, iron (III), iron oxide.

Introduction

Industrial systems that use water are often challenged by problems caused by the presence of both soluble and insoluble impurities. These impurities, organic and inorganic, if not properly treated, result into the formation and deposition of unwanted materials on heat exchangers, pumps, pipes, and other equipment surfaces. The problems caused by unwanted materials (e.g., mineral scales, corrosion products, suspended matter, biological mass) include reduced heat transfer, equipment corrosion, pre-mature equipment replacement, and increased operating costs. Greater water conservation has been a driver for operating industrial water systems at higher cycles of concentrations, thereby increasing the potential for deposit buildup on heat exchanger surfaces. Thus, effective deposit control is paramount to minimizing operating costs for industrial water systems.1

A large variety of deposit control additives have been developed and are currently used to combat the challenging problems encountered in industrial water systems. Corrosion and microbiological problems are controlled by using corrosion inhibitors and biocides, respectively. The most promising scale control method involves adding sub-stoichiometric dosages (typically a few parts per million) to the feed water of either non-polymeric (e.g., phosphonates, polyphosphate) or polymeric (e.g., carboxylate containing homopolymers, copolymer containing carboxylic acid and well as other functional groups) water soluble additives.

It is well known for polymers containing different functional group (e.g., carboxylic acid, sulfonic acid, s-acrylamide), that inhibiting scale forming salt precipitation is dependent on (a) polymer architecture (e.g., ionic charge, monomer size, monomer ratio, MW) and (b) the scaling salts being formed (e.g., CaCO₃, CaSO₄.2H₂O, Ca₃(PO₄)₂, CaF₂). In addition, DCP hydrolytic and thermal stability as well as other factors (e.g., water chemistry and other treatment chemicals
concentrations & types including flocculants, corrosion inhibitors, biocides), are known to impact the efficient operation of industrial water systems.

Factors for selecting additives (polymer and non-polymeric) include system operating conditions (e.g., cycles of concentration, pH, temperature); additive hydrolytic and thermal stability; inhibitor interactions with hardness ions and biocides; the presence (or not) of soluble impurities (e.g., Fe(III), Al(III), polymeric flocculant); and insoluble impurities (e.g., corrosion products, clay, silt). It is generally recognized that carboxylic acid containing homopolymers (e.g., polyacrylic acid, polymaleic acid, polyaspartic acid) are effective inhibitors for CaCO₃, CaSO₄,2H₂O, CaF₂ and clay dispersants but also exhibit mediocre to good performance as Ca₃(PO₄)₂, Ca-HEDP, and Ca-AMP inhibitors. On the other hand, polymers containing different monomers and functional groups (e.g., polyacrylic acid [-COOH]; 2-acrylamido-2-methylpropane sulfonic acid [-HSO₃], sulfonated styrene [styrene-SO₃H], substituted acrylamide [s-CON(R₁, R₂)]) are excellent calcium phosphate/phosphonate inhibitors and Fe₂O₃ dispersants as well as effective metal ions (Al, Fe, Mn) stabilizers and metal hydroxides dispersants.⁷,⁸

The purpose of this paper is to evaluate the laboratory screening test performance data (i.e., calcium phosphate inhibition, calcium carbonate inhibition, and iron oxide dispersion) of a ≈2k MW polyacrylate (PAA), a high performance acrylate terpolymer (ATP), and a PAA/ATP (1:1 active solids basis) blend. The goal is to provide water technologists with information that will help facilitate DCP selection based on performance and treatment program objectives.

### Experimental

**Materials Used and Polymers Evaluated**

Reagents grade chemicals and grade A glassware were used. The preparation of stock solutions (i.e., calcium chloride, magnesium chloride, disodium hydrogen phosphate, sodium carbonate, sodium chloride, sodium sulfate, and sodium bicarbonate) using distilled water as well as the test procedures and associated analyses were described previously;⁹ other details appear in the text below. The polymers tested are listed in Table 1. The stock solutions of these polymers were prepared in distilled water on a dry weight basis.

<table>
<thead>
<tr>
<th>Product</th>
<th>Composition</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-7028*</td>
<td>Water polymerized 2.3k MW poly(acrylic acid)</td>
<td>PAA</td>
</tr>
<tr>
<td>K-798*</td>
<td>Water polymerized &lt;15k MW poly(acrylic acid: 2-acrylamido-2-methylpropane sulfonic acid: sulfonated styrene) or “AA/SA/SS”</td>
<td>ATP</td>
</tr>
<tr>
<td>Blend</td>
<td>1:1 active solids blend of PAA &amp; ATP (two polymer blend)</td>
<td>TPB</td>
</tr>
</tbody>
</table>

* Carbosperse™ K-700 polymer supplied by Lubrizol Advanced Materials, Inc.

### Calcium Phosphate Inhibition

Supersaturated solutions of calcium phosphate for precipitation experiments were prepared, by adding a known volume of phosphate stock solution to the thermostated-glass cell maintained at constant temperature, containing a known concentration of polymer in distilled water. After temperature equilibration, a known volume of stock calcium chloride solution was added making up the total volume to 600 mL. Spontaneous precipitation was induced by adjusting
the 600 mL acid solution to pH 8.50 with 0.10M NaOH. During each experiment, the test solution pH was maintained at 8.50 ± 0.01 with 0.10M NaOH solution using the pH-stat unit (Model 600 series, Metrohm Brinkmann Instruments, NY) equipped with a combination electrode. The pH electrode was calibrated before each experiment with standard buffers. Unless specified, the test conditions for calcium phosphate inhibition were 140 mg/L Ca, 9.0 mg/L phosphate, pH 8.50, 50°C). Experiments involving Fe(III) were performed by adding FeCl₃ solution to phosphate solution containing polymer, before adding the stock calcium chloride solution.

The progress of precipitation process was determined by spectrophotometric analysis of filtered (0.45 micron, Millipore Corporation) aliquot of the test solution for the phosphate ion. The efficacy of polymer as a calcium phosphate inhibitor was calculated using the following equation:

\[
\text{% Inhibition} = \frac{[\text{PO}_4^{\text{sample}}] - [\text{PO}_4^{\text{control}}]}{[\text{PO}_4^{\text{initial}}] - [\text{PO}_4^{\text{control}}]} \times 100
\]  

(1)

Where the terms above are as follows:

- Inhibition (%) = %I
- \([\text{PO}_4^{\text{sample}}]\) = PO₄ concentration in the presence of inhibitor at the end of the test
- \([\text{PO}_4^{\text{control}}]\) = PO₄ concentration in the absence of inhibitor at the end of the test
- \([\text{PO}_4^{\text{initial}}]\) = PO₄ concentration at the beginning of the test

**Calcium Carbonate Inhibition**

The efficacy of polymer as calcium carbonate inhibitor was tested using the following test procedure. To a 125 mL glass bottle containing distilled water, known volumes of stock solutions of sodium bicarbonate, sodium carbonate, and polymer were added with stirring followed by the addition of known volume of calcium chloride stock solution to create a 100 mL solution. The 100 mL test solution (56x calcite saturation or LSI 1.89) composition was 560 mg/L Ca as CaCO₃, 630 mg/L HCO₃ as CaCO₃, and 30 mg/L CO₃ as CaCO₃ (≈ pH 8.3) with 0.25 to 5.0 ppm polymer. The bottles were capped and stored in water bath maintained at 66°C for 24 hr. The progress of precipitation process was determined by titrating the filtered (0.22 micron, Millipore Corporation) aliquot of the test solution with standard EDTA solution for calcium ion. The efficacy of polymer as a calcium carbonate inhibitor was calculated using the following equation:

\[
\text{% Inhibition} = \frac{[\text{Ca}^{2+}]_{\text{sample}} - [\text{Ca}^{2+}]_{\text{control}}}{[\text{Ca}^{2+}]_{\text{initial}} - [\text{Ca}^{2+}]_{\text{control}}} \times 100
\]  

(2)

Where the terms above are as follows:

- Inhibition (%) = %I
- \([\text{Ca}^{2+}]_{\text{sample}}\) = Ca²⁺ concentration in the presence of inhibitor at the end of the test
- \([\text{Ca}^{2+}]_{\text{control}}\) = Ca²⁺ concentration in the absence of inhibitor at the end of the test
- \([\text{Ca}^{2+}]_{\text{initial}}\) = Ca²⁺ concentration at the beginning of the test
Iron Oxide Dispersion

A known amount (0.12 g) of iron oxide was added to 800 mL beaker containing simulated industrial water (600 mL) and known amount of polymer (dispersant) solution. The simulated industrial water used in the dispersion tests was made by mixing standard solutions of calcium chloride, magnesium chloride, sodium sulfate, sodium chloride, and sodium bicarbonate. The simulated industrial water composition was 100 mg/L Ca, 30 mg/L Mg, 314 mg/L Na, 264 mg/L Cl, 570 mg/L SO₄, 60 mg/L HCO₃, and pH 7.6 to 7.8. All dispersion tests were run at room temperature (≈22ºC).

A typical test run consists of six simultaneous experiments using a gang-stirrer set to 110 revolutions per minute. At known time intervals, transmittance readings (%T) were taken with Brinkmann® Probe Colorimeter equipped with 420 nm filter. The absorbance of several filtered (0.22 micron) suspensions with low to high %T was measured at 420 nm; the absorbance contribution due to dissolved species was insignificant (<3%). Polymer performance as percent iron oxide dispersed (%D) was calculated based on %T readings taken as a function of time and using the equation below which includes an adjustment for readings obtained in the absence of polymer.

\[
%D = [100 - (1.11 \times \% \text{ transmittance})]
\]

The data presented herein had good reproducibility (±5% or better). Polymer performance was determined by comparing the %D values of the slurries containing polymer to the control (no polymer). Therefore, higher %D values indicate greater dispersion.

Results and Discussion

Calcium Phosphate Inhibition

Polymer Dosage Effect

A polymer’s ability to inhibit calcium phosphate is very important aspect of phosphate and phosphonate-based treatment programs. Figure 1 shows percent inhibition (%I) as a function of polymer dosage. As indicated, PAA exhibits poor (<20% inhibition) calcium phosphate (Ca/P) inhibition regardless of the dosage. For example, the %I value obtained for PAA at 7.5 ppm is 12% compared to 17% obtained at 15 ppm. Increasing PAA concentration from 15 to 20 ppm shows only a slight Ca/P inhibition improvement (from 17% to 20%). The poor PAA Ca/P inhibition at higher concentrations may in part be attributed to poor PAA tolerance with calcium ion.

Figure 1 shows that 5.0 ppm ATP provides poor inhibitory activity (<10% inhibition). However, ATP performance is substantially improved (63%) at 6.5 ppm and exceeds 95% at 7.5 ppm compared to only 5% inhibition for the same PAA dosage. This suggests that incorporating co-monomers containing a strong acid group (e.g., --SO₃H) and hydrophobic group (e.g., sulfonated styrene) in ATP greatly increases the inhibition effect of the polymer. The ability of a polymer to provide superior performance at low dosage is a highly desirable characteristic.
Polymer Blend Performance

In order to evaluate the influence of polymer blending, a series of precipitation experiments were conducted using varying dosages of a PAA/ATP (1:1 active polymer basis) blend (TPB). The calcium phosphate inhibition results shown in Figure 1 indicate:

- TPB performance increases with increasing dosages.
- The TBP performance is better than would be expected based on the performance for the blend component especially the PAA which performs poorly by itself.

The improved TPB performance observed in the present investigation is consistent with a previous study on the evaluation of polymer blends as stabilizers for amorphous calcium phosphate.10

Effect of Fe$^{3+}$

Soluble iron, the ferrous ion (Fe$^{2+}$), is often encountered in natural water systems at low concentrations (usually < 3 ppm) or as a result of the iron corrosion from system piping, well heads, or other equipment. Upon oxidation, the ferric ion (Fe$^{3+}$) may “tie up” or deactivate polymer performance as a scale inhibitor. It is therefore important to evaluate a polymer’s efficacy as a calcium phosphate inhibitor in the presence of Fe$^{3+}$.

Figure 2 presents the effect of 1.0 ppm Fe$^{3+}$ on the performance of 10 ppm dosages of PAA, ATP, and TPB. As shown, adding 1.0 ppm Fe$^{3+}$ has a negligible impact on ATP performance. For example, %I values obtained for 10 ppm ATP in the presence of 0 and 1.0 ppm Fe$^{3+}$ are 99% and 97%, respectively. However, 1.0 ppm Fe$^{3+}$ has a pronounced antagonistic effect on the performance of PAA and TPB; PAA lost almost 50% of its inhibitory activity and TPB performance decreases >35%.
Calcium Carbonate Inhibition

Calcium carbonate (CaCO$_3$) is one of the most commonly encountered scale deposits. CaCO$_3$ is found in different crystalline forms in the following order of increasing solubility: calcite, aragonite, vaterite, CaCO$_3$ monohydrate and CaCO$_3$ hexahydrate. Calcite, the thermodynamically most stable polymorph of CaCO$_3$, forms tenaciously adhering, hard mineral deposits. Precipitation and stabilization of CaCO$_3$ polymorphs depends on system conditions (i.e., supersaturation level, pH, temperature, pressure, and the concentrations and architecture of the additives).

Figure 3 presents CaCO$_3$ inhibition data as a function of PAA, ATP, and TPB dosages leading to several observations discussed below.

1. Relatively small PAA dosages significantly inhibit CaCO$_3$ precipitation as summarized in the table below:

<table>
<thead>
<tr>
<th>PAA Dosage</th>
<th>0.5 ppm</th>
<th>1.0 ppm</th>
<th>3.0 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$ Inhibition</td>
<td>56%</td>
<td>71%</td>
<td>85%</td>
</tr>
</tbody>
</table>

2. ATP does not perform as well as PAA. For example, %I values obtained in the presence of 3.0 ppm polymer are 85% and 65% for PAA and ATP, respectively indicating that incorporating co-monomers containing non-carboxyl groups (e.g., SO$_3$H, bulkier and hydrophobic styrene) reduces ATP CaCO$_3$ inhibition performance. The results also suggest that --COOH group present in PAA strongly interacts with Ca present in CaCO$_3$ crystallites formed during the precipitation process.

3. TPB which lags but closely parallels the PAA performance. Thus, adding ATP to CaCO$_3$ supersaturated solution does not deleteriously affect the performance of PAA.
Iron Oxide Dispersion

Among many dissolved impurities present in natural waters, iron-based compounds present one of the most common and challenging problems to the efficient operation of industrial water systems. Sources of iron-based impurities include boiler condensate, corrosion products (e.g., heat exchangers, pipes, pumps) biological activity (the transformation of iron during bacterial processes), and water treatment residuals or by products (e.g., excessive iron-based flocculants). Regardless of the source, soluble iron can and does precipitate under certain conditions to form troublesome scales and deposits [e.g., $\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, $\text{Fe(OH)}_3$, $\text{FePO}_4$]. For this reason, deposit control polymers are used to keep iron oxide particles dispersed and transported in boiler and re-circulating cooling water systems. This dispersion activity results from the adsorption of polymer onto surface of iron oxide particles, thereby changing particle charge characteristics and minimizing agglomeration.

ATP, PAA, and TPB as iron oxide dispersants were investigated by conducting a series of dispersion experiments as a function of time and polymer dosage. Figure 4 presents % iron oxide dispersed (%D) as a function of time and ATP dosage. It can be seen that %D value increases sharply in the first 30 min and slows down thereafter. The sharp increase in the first 30 minutes reflects fast ATP adsorption on iron oxide particles.

ATP iron oxide dispersion performance indicates a ‘normal’ dose-response relationship; i.e., performance increases with polymer dosage. For example, 0.25 ppm ATP shows mediocre performance (<50% at 3 hr) but doubling ATP dosage (to 0.50 ppm) clearly improves performance (>60% at 3 hr) and performance reaches ≈80% at 1.0 ppm ATP. However, increasing ATP dosage above 1.0 ppm (i.e., from 1.0 to 1.5 to 2.0 ppm) has an insignificant iron oxide dispersion improvement. The data suggest that ATP adsorption on iron oxide is essentially complete at ≈1.0 ppm dosage indicating that ATP is a highly effective iron oxide dispersant.
PAA efficacy as an iron oxide dispersant was investigated by carrying out a series of experiments as a function of time and dosage. The PAA iron oxide dispersion data shown graphically in Figure 5 indicate:

- Dispersion values increase with increasing time.
- Dispersion values increase with increasing PAA dosage and peak at ≈1.0 ppm.
- PAA compared to ATP exhibits relatively poor performance. For example, the %D value obtained at 3 hr for PAA is <30% compared to >80% obtained for ATP. The relatively poor PAA performance compared to ATP may be attributed to poor PAA adsorption on iron oxide particles and/or poor interaction of –COOH group with Fe on iron oxide particles.
Figure 6 presents TPB iron dispersion data. It is clearly evident that TPB performance depends on both the kinetics (contact time) and dosage; performance increases with both increasing contact time and dosage providing an optimum performance at 3 hr and 1.0 ppm dosage. The relatively poor TPB performance may be explained in terms of competitive adsorption due to polymer architecture (polymer composition and MW). PAA, a low MW (2.3k) polymer, diffuses through the solution faster and adsorbs first (before ATP) on iron oxide particles. On the other hand, ATP is a relatively high (<15k) MW polymer and its adsorption is hindered by PAA already adsorbed on the iron oxide particles. A MW effect for poly(acrylic acid) and acrylic acid-based copolymers on iron oxide dispersion has been reported.\textsuperscript{11} Results of the investigation herein reveal that iron oxide dispersant performance decreases with increasing polymer MW in the range 2,000 to 20,000. The poor performance shown by high MW polymer is due to steric hindrance in the adsorption of polymer to iron oxide particles. Similar MW dependence on polymer performance as inhibitors for calcium phosphate, calcium carbonate, calcium phosphonate, and calcium sulfate dihydrate has been reported previously.\textsuperscript{12-16} Among the family of AA/SA/SS terpolymers, a commercially available lower MW version of ATP provides better iron oxide dispersion than the material evaluated herein.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure6}
\caption{Iron Oxide Dispersion for TPB as a Function of Dosage & Time}
\end{figure}

Figure 7 shows the dispersion data collected at 3 hr and in the presence of 1.0 ppm of ATP, PAA, and TPB. Compared to PAA, ATP exhibits excellent iron oxide dispersion. A similar performance trend comparing PAA to ATP was also observed for calcium phosphate inhibition.\textsuperscript{12} In addition, an opposite trend in polymers performance was observed for calcium carbonate inhibition suggesting that polymer performance as scale inhibitor and dispersant depends on polymer architecture and scaling salts being inhibited.
Summary

Water technologists design treatment programs incorporating combinations of components that provide synergistic and cost-effective properties to control corrosion, microbiological fouling, and scaling. Using multiple DCPs as components of treatment programs is a common practice based on the expectation of synergism and optimizing cost vs. performance. A series of laboratory screening tests were used to evaluate the performance of a ≈2k MW PAA, a high performance ATP, and a PAA/ATP (1:1 on active solids basis) blend (TPB) lead to the following performance ranking:

<table>
<thead>
<tr>
<th>Screening Test / Performance Parameter</th>
<th>Best</th>
<th>Mid-Range</th>
<th>Worst</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Calcium phosphate (Ca/P) inhibition</td>
<td>ATP</td>
<td>&gt; TPB</td>
<td>&gt;&gt;&gt; PAA</td>
</tr>
<tr>
<td>• Ca/P inhibition in presence of soluble iron</td>
<td>ATP</td>
<td>&gt;&gt; TPB</td>
<td>&gt; PAA</td>
</tr>
<tr>
<td>• Calcium carbonate inhibition</td>
<td>PAA</td>
<td>&gt; TPB</td>
<td>&gt; ATP</td>
</tr>
<tr>
<td>• Iron oxide dispersion</td>
<td>ATP</td>
<td>&gt;&gt; TPB</td>
<td>&gt; PAA</td>
</tr>
</tbody>
</table>

Other DCPs and/or ratios of homopolymers and copolymers may lead to alternative performance rankings. In addition, water treatment formulations must take into consideration both the unit cost of components as well as the working capital and operating cost implications of maintaining and using multiple and/or a wide range of water treatment formulating components.
Acknowledgements

The authors thank Scranton Associates’ Robert R. Cavano for his questions regarding the performance, economics, and wisdom of combining homopolymers and copolymers as components of water treatment formulations that were the key driver for this paper.

References


